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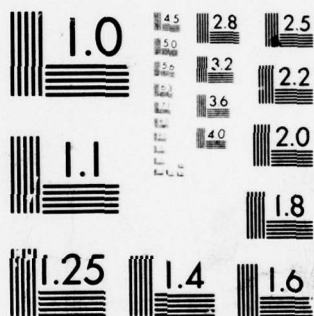
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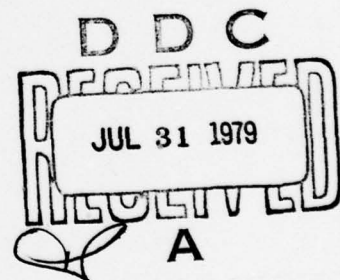
ELECTROCHEMICAL POLYMERIZATION
AND DEPOSITION ON CARBON FIBERS

by

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July 15, 1979



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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The electrochemical polymerization on carbon fibers of a variety of monomers having different functional groups has been investigated. The objective was to demonstrate the effect of such polymer coating on the properties of polymer composites prepared from the coated fibers. The electropolymerization of novel monomers encountered in this study was pursued in some detail. In addition to usual vinyl polymerizations, some novel cyclic monomers were identified as capable of producing the desired polymer layer on fibers under appropriate polymerization conditions. In many instances, grafting of the		

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surface polymer to the fiber was observed. ←

Composite specimens were prepared by the incorporation of the coated fibers in an epoxy matrix. It was demonstrated that the effect of electropolymerization on the interfacial properties of the resulting composite was manifested in variations of the measured interlaminar shear and impact strengths of the composite specimens. The increase or decrease in interlaminar shear was accompanied by the usually observed reverse change in impact strength. It was significant, therefore, when in exception to this general trend, it was also found that both interlaminar shear and impact strengths could simultaneously be increased. Implicit in this finding is the contribution of the electrochemically formed interlayer to one or more of the toughening mechanisms available to fiber reinforced composites.

The development and standardization of an electrodeposition technique for the interphase modification of carbon fiber composites was also undertaken. The effect of the interphase polymer was studied through variations in the impact, interlaminar shear, and flexural strengths of composites fabricated with the coated fibers, in comparison to those of composites fabricated using commercially treated and untreated fibers.

Carbon fibers running continuously through an electrolytic cell as the anode were coated with a variety of maleic anhydride copolymers under optimum cell operating conditions. The coated fibers were then embedded in an epoxy matrix. The unidirectional composites thus prepared were tested for impact, interlaminar shear, and flexural strengths. Fortafil CG-3 fiber, free of commercial surface treatments, was used in these experiments. The copolymers employed were a series of styrene-co-maleic anhydride, α -olefin-co-maleic anhydride, methyl vinyl ether-co-maleic anhydride, and ethylene-co-acrylic acid.

The introduction of a polymer interphase results in significant improvements in composites when the coated fibers are incorporated in an epoxy matrix. The measured interlaminar shear, impact, and flexural strengths show such improvements conclusively. The molecular weight, chemical composition, and cross-linking of the interphase polymer are molecular parameters that control the degree of improvement achieved in strength and toughness of the composite.

Electrochemical polymerization and deposition offer a new route for coating carbon fibers prior to embedding them in a polymer matrix. The potential value of these techniques to composite property modification was thus amply demonstrated.

The polymerization of monomers through acetylenic and nitrile groups has been studied. In the cathodic polymerization of phenylacetylene in dimethylformamide, an anionic polymerization mechanism is indicated. The polymer of molecular weight ~ 3000 has been fractionated and the fractions characterized by ir, uv, and nmr spectroscopy. Evidence is presented for a conjugated polyene structure formed from cis and trans structural units combined in a predominantly head-to-tail fashion. Similarly, the polymerization of benzonitrile in dimethylformamide at the cathode leads to a polymer with conjugated $-C=N-$ bonds. Mass spectroscopy did not reveal the presence of any cyclic trimer of benzonitrile. Infrared absorption bands at 1605 cm^{-1} and 1520 cm^{-1} established the formation of $-C=N-$ conjugation in polybenzonitrile.

Copolymers of phenylacetylene and benzonitrile were observed to form in the cathode compartment in a manner similar to polyphenylacetylene. It was observed that while initial monomer ratios varied greatly, elemental analysis indicates incorporation of monomers in approximately one to one ratio in the resulting copolymer. This observation and the very low molecular weights of the copolymer products suggest that addition of a benzonitrile unit inhibits further polymerization.

The electropolymerization of monomers containing an aziridiny ring was shown to polymerize at the anode, the resulting polymers having a polyamine

backbone structure. A cationic mechanism of polymerization was suggested. In addition, a difunctional monomer 2-(1-aziridiny)ethyl methacrylate, was shown to undergo selective polymerizations of the aziridiny group at the anode and the vinyl group at the cathode, leaving unreacted vinyl and aziridiny groups, respectively, in the resulting polymers.

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Electrochemical Polymerization
and Deposition on Carbon Fibers

by

R. V. Subramanian

The work done under contract N000-75-C-0792 is reported below.

The primary objective of this investigation was interphase modification in graphite fiber composites by polymer coating of the reinforcing fibers, prior to composite fabrication, by electrochemical techniques.

The investigation undertaken in pursuit of this objective developed techniques of electropolymerization on graphite fibers. The occurrence of polymer grafting to the fibers could be established. Indications were obtained of the influence of the graphite fiber surface on the stereochemical configuration of poly(methyl methacrylate) formed electrolytically on the fiber. In addition to vinyl polymerization, a number of novel electropolymerizations, previously unreported, were found to occur. These were investigated to establish the mechanism of electropolymerization and the structure of the polymer formed. The electroinitiated polymerizations of aziridines, benzonitrile, phenylacetylene, and 3-aminophenylacetylene belong to this group; for the first time the occurrence of electropolymerization through the opening of the cyclic functional group, aziridine, and of $C\equiv N$ and $C\equiv C$ bonds was established.

The properties of composites prepared from the polymer coated graphite fiber were studied. The effect of the interphase polymer was found to be manifested in modification of interlaminar shear and impact strengths. The formation of interphase polymer by electrodeposition of ionizable polymers was also studied and its effect on composite properties determined. The molecular parameters that control the degree of improvement in strength and toughness were identified. Most importantly, it was found possible to achieve simultaneous improvements in interlaminar shear and impact strengths of graphite composites.

This research represents a major advance in interphase modification in graphite composites and has opened up a new area of investigation into the chemical and mechanical requirements of the fiber-matrix interphase for optimum reinforcement. The results are reported in the following publications.

Publications.

1. R. V. Subramanian, "Electroinitiated Polymerization on Electrodes", Adv. Polym. Sci, 33, (1979).
2. R. V. Subramanian, James J. Jakubowski, "Electropolymerization on Graphite Fibers", Polym. Eng. Sci, 18, 590 (1978).
3. R. V. Subramanian, V. Sundaram, A. K. Patel, "Electrodeposition of Polymers on Graphite Fibers: Effects on Composite Properties", SPI Reinf. Plast./Composites Inst. (1978), 20F.
4. R. V. Subramanian, J. J. Jakubowski, F. D. Williams, "Interfacial Aspects of Polymer Coating by Electropolymerization", J. Adhesion, 9, 185 (1979).

5. R. V. Subramanian, B. K. Garg, "Electroinitiated Polymerization of Benzonitrile", Polymer Bulletin, 1, 421 (1979).
6. James J. Jakubowski, R. V. Subramanian, "Electroinitiated Polymerization and Copolymerization of Phenylacetylene", Polymer Bulletin (Communicated).
7. James J. Jakubowski, R. V. Subramanian, "Electroinitiated Polymerization of Aziridines", Polymer (Communicated).
8. R. V. Subramanian, J. J. Jakubowski, "Interphase Resin Modification in Graphite Composites" in "Resins for Aerospace", ACS Advances in Chemistry Series, (1979), to be published.

Theses

1. James Jerome Jakubowski, "Interface Modification of Carbon Fiber Composites by Electropolymerization", M.S. 1976.
2. Viswanath Sundaram, "Electrodeposition of Polymers on Carbon Fibers: Effects on Composite Properties", M.S. 1977.
3. James Jerome Jakubowski, "Electrochemical Polymerization and Deposition on Carbon Fiber", Ph.D. 1979.

The abstracts of these publications are given in succeeding pages.

Electroinitiated Polymerization on Electrodes

R. V. Subramanian
Adv. Polym. Sci., 33, (1979)

ABSTRACT

Electroinitiated polymerization reactions leading to the formation of polymer on electrode surfaces - as distinguished from that in the bulk of the electrolytic solution - are discussed here. The structure and morphology of the polymer, and its bonding and adhesion to the electrode surface are examined in addition to the mechanisms of polymerization. The formation of adherent coatings on electrodes discussed in this manner is that of polymers from not only vinyl monomers, but also from phenols, acrolein, benzonitrile, polyimide intermediates and phenylacetylene. The novel use of carbon fiber electrodes in electroinitiated polymerization is introduced and its significance to interphase modification in carbon fiber composites is brought out. With continuing advances in techniques for the study of the formation, control, and properties of polymer films on electrodes, concurrent progress in investigation of surface coatings and graphite composites is indicated.

Electropolymerization on Graphite Fibers

R. V. Subramanian and James J. Jakubowski
Polym. Eng. Sci. 18, 590 (1978)

ABSTRACT

The electrodic polymerization on graphite fibers of a variety of monomers having different types of functional groups has been investigated. In addition to vinyl polymerization, some novel polymerization of cyclic functional groups have been conducted under appropriate polymerization conditions. In many instances, the grafting of the surface polymer to the fiber has been confirmed. The stereochemical configuration of poly(methyl methacrylate) resulting from electropolymerization was measured, but conclusive evidence could not be obtained for the occurrence of stereo-regulation in electrochemical polymerization on graphite fiber surface. Composite specimens were prepared by the incorporation of the coated fibers in an epoxy matrix. It was demonstrated that the effect of electropolymerization on the interfacial properties of the resulting composite was manifested in variations of the measured interlaminar shear and impact strengths of the composite specimens. The increase or decrease in interlaminar shear was accompanied by the usually observed reverse change in impact strength. In exception to this general trend, it was also indicated that the shear and impact strengths could simultaneously be increased. Implicit in these findings is the contribution of the electrochemically formed interlayer to one or more of the toughening mechanisms that are available to fiber reinforced composites. The potential value of interphase modification by electrochemical polymerization is thus clearly indicated.

Electrodeposition of Polymers on Graphite Fibers:
Effects on Composite Properties

R. V. Subramanian, V. Sundaram and A. K. Patel
SPI Reinf. Plast./Composites Inst. (1978, 20F)

ABSTRACT

An electrodeposition technique has been developed for interface tailoring in graphite fiber composites. Graphite fibers running continuously as the anode through an electrolytic cell were coated with a variety of copolymers carrying carboxyl functional groups. Fortafil CG-3 fiber, free of commercial surface treatments, was used in these experiments. The copolymers employed were a series of styrene-*co*-maleic anhydride, α -olefin-*co*-maleic anhydride, methyl vinyl ether-*co*-maleic anhydride, and ethylene-*co*-acrylic acid polymers. Unidirectional composite specimens were prepared by embedding the coated fibers in an epoxy matrix, and the effect of the interphase polymer was studied through variations in their impact, interlaminar shear, and flexural strengths in comparison to those of composites fabricated from commercially treated and untreated fibers. It is found that the introduction of the polymer interphase results in significant improvements in composite properties and that the extent of improvement is controlled by the nature of the polymer interphase. The molecular weight, chemical composition, and crosslinking of the interphase polymer are some of the molecular parameters modifying the effects observed. It is concluded that the electrodeposition of polymers on graphite fibers provides an effective method of optimizing composite strength and toughness through the introduction of an interlayer of variable properties.

Interfacial Aspects of Polymer Coating by Electropolymerization

R. V. Subramanian, James J. Jakubowski and F. D. Williams
J. Adhesion, 1978, Vol. 9, pp. 185-195

ABSTRACT

Polymer coatings were produced on graphite fiber electrodes by electro-initiated polymerization in an electrolytic cell containing monomer. The adhesion of the coated graphite fibers to an epoxy matrix has been measured by single fiber pull-out tests. The measured values of the pull-out force, and scanning electron micrographs of pulled-out fibers reveal three modes of failure and degrees of adhesion independent of the type of polymer coating. It is seen that the initial formation of a resin cone on the embedded fiber contributes significantly to the measured values of the pull-out force for fine, 5-10 μm carbon fibers but not for larger diameter ($>50 \mu\text{m}$) fibers. The effect of the surface treatment on the interfacial properties of composites prepared from the coated fibers was manifested in variations of the interlaminar shear and impact strengths of epoxy composite specimens which were sensitive to the type of coating polymer. Polymer coating of carbon fibers by electodic processes is thus seen as a promising approach to the study of the polymer interphase in carbon fiber reinforced composites.

Electroinitiated Polymerization of Benzonitrile

R. V. Subramanian and B. K. Garg
Polymer Bulletin 1, 421-426 (1979)

The electroinitiated polymerization of benzonitrile yields a linear conjugated polymer, $[(C_6H_5)C=N]_n$. An anionic mechanism of polymerization is indicated.

Electroinitiated Polymerization and Copolymerization of Phenylacetylene

James J. Jakubowski and R. V. Subramanian
Polymer Bulletin (Communicated)

ABSTRACT

A linear conjugated polymer $[\text{C}_6\text{H}_5)\text{C}-\text{CH}]_n$, with a *trans* rich, *cis-trans* copolymer structure results from the electropolymerization of phenylacetylene.

Electroinitiated Polymerization of Aziridines

James J. Jakubowski and R. V. Subramanian
Polymer (Communicated)

ABSTRACT

The electroinitiated polymerization of N-(2-hydroxyethyl) ethylaneimine is shown to occur at the anode by a cationic mechanism. A difunctional monomer, 2-(1-aziridiny)ethyl methacrylate has been selectively polymerized, through the vinyl group at the cathode, and through the aziridiny group at the anode. The structure of the polymers has been studied by ir and nmr spectroscopy.

Interphase Resin Modification in Graphite Composites

R. V. Subramanian and James J. Jakubowski
in "Resins for Aerospace",
ACS Advances in Chemistry Series, (1979), to be published.
ABSTRACT

Interphase modification through electropolymerization and electrodeposition, such as that of N-2-hydroxyethyl ethyleneimine, has been shown to be effective in improving composite shear strength and toughness. Studies with model compounds such as phenylacetylene and benzonitrile confirm the occurrence of electroinitiated polymerization on graphite fibers through the $C\equiv C$ or $C\equiv N$ bonds in nitrile or acetylene terminated polyimide intermediates. The concept of interphase modification has been expanded by the application of electrochemical coating of carbon fiber to reduce the potential for release of conductive fiber fragments from graphite composites. Polyimide precursors were formed electrochemically on carbon fibers. Thermogravimetric analysis was used to measure the significant effects of the coatings on the thermal oxidative behavior of the system components. Electrochemical polymerization thus offers a new route for coating carbon fibers prior to embedding them in a polymer matrix. The potential value of these techniques to composite property modification was amply demonstrated.

Thesis: Interface Modification of Carbon Fiber Composites
by Electropolymerization

James Jerome Jakubowski, M.S.
Washington State University, 1976

ABSTRACT

Interface tailoring in carbon fiber-polymer composites by means of electrochemical polymerization has been investigated. It was expected that fiber-matrix adhesion and composite mechanical properties can be modified by the electrochemical formation of polymer layers of varying structure and properties on carbon fibers prior to their incorporation in a polymer matrix.

Techniques were developed first for producing thin polymer coatings on carbon fibers by using the latter as electrodes in an electrolytic cell containing the monomer. A variety of vinyl and cyclic monomers having different types of functional groups were identified as capable of producing the desired polymer layer on the fibers under appropriate polymerization conditions. It was shown that, in many instances, the surface polymer was chemically bonded, i.e., grafted, to the carbon fiber.

Composite specimens were prepared by the incorporation of the coated fibers in an epoxy matrix. It was demonstrated that, in fact, the effect of the surface treatment on the interfacial properties of the resulting composite was manifested in variations of the measured interlaminar shear and impact strengths of the composite specimens. The increase in interlaminar shear was considered to be the result of improved fiber-matrix adhesion when compared to composite specimens prepared from untreated carbon fiber. The corresponding reversed trend in impact strength values was hence attributed to the effect of excessive fiber-matrix adhesion in causing brittle failure of the composite. It was significant, therefore, when in exception to this general trend, it was also found that both interlaminar shear and impact strengths could simultaneously be increased. Implicit in this finding is the contribution of the electrochemically formed interlayer to one or more of the toughening mechanisms that are available to fiber reinforced composites. The potential value of interface modification by electrochemical polymerization in optimizing both interlaminar shear and impact strengths of carbon fiber composites is thus clearly indicated.

Thesis: Electrodeposition of Polymers on Carbon Fibers:

Effects on Composite Properties

Viswanath Sundaram, M.S.
Washington State University, 1977

ABSTRACT

The primary objective of this investigation was the development and standardization of an electrodeposition technique for the interface modification of carbon fiber composites. The effect of the interphase polymer was studied through variations in the impact, interlaminar shear, and flexural strengths of composites fabricated with the coated fibers, in comparison to those of composites fabricated using commercially treated and untreated fibers.

Carbon fibers running continuously through an electrolytic cell as the anode were coated with a variety of maleic anhydride copolymers under optimum cell operating conditions. The coated fibers were then embedded in an epoxy matrix. The unidirectional composites thus prepared were tested for impact, interlaminar shear, and flexural strengths. Fortafil CG-3 fiber, free of commercial surface treatments, was used in these experiments. The copolymers employed were a series of styrene-co-maleic anhydride, α -olefin-co-maleic anhydride, methyl vinyl ether co-maleic anhydride, and ethylene-co-acrylic acid.

Scanning Electron Microscopy studies of the fiber surface showed the uniformity of polymer layer formed on the fibers with the alkene-maleic anhydride copolymers. The methyl vinyl ether-maleic anhydride copolymers were observed to form rougher coatings. Subsequent mechanical testing showed that the uniformly coated fibers formed composites of better strength and toughness.

The introduction of a polymer interphase results in significant improvements in composites when the coated fibers are incorporated in an epoxy matrix. The measured interlaminar shear, impact, and flexural strengths show such improvements conclusively. The molecular weight, chemical composition, and crosslinking of the interphase polymer are molecular parameters that control the degree of improvement achieved in strength and toughness of the composite.

Based on the results of the investigation, it is concluded that electrodeposition of polymers on carbon fibers provides an effective method of interface modification to produce a complex interlayer in graphite fiber composites. The extent of the improvement of the composite properties is controlled by the nature of the polymer interphase.

Thesis: Electrochemical Polymerization and Deposition on Carbon Fibers

James Jerome Jakubowski, Ph.D.
Washington State University, 1979

ABSTRACT

The electrodic polymerization on carbon fibers of a variety of monomers having different functional groups has been investigated. The objective was to demonstrate the effect of such polymer coating on the properties of polymer composites prepared from the coated fibers. The electropolymerization of novel monomers encountered in this study was pursued in some detail. In addition to usual vinyl polymerizations, some novel cyclic monomers were identified as capable of producing the desired polymer layer on fibers under appropriate polymerization conditions. In many instances, grafting of the surface polymer to the fiber was observed.

Composite specimens were prepared by the incorporation of the coated fibers in an epoxy matrix. It was demonstrated that the effect of electropolymerization on the interfacial properties of the resulting composite was manifested in variations of the measured interlaminar shear and impact strengths of the composite specimens. The increase or decrease in interlaminar shear was accompanied by the usually observed reverse change in impact strength. It was significant, therefore, when in exception to this general trend, it was also found that both interlaminar shear and impact strengths could simultaneously be increased. Implicit in this finding is the contribution of the electrochemically formed interlayer to one or more of the toughening mechanisms available to fiber reinforced composites.

Phenylacetylene was shown to polymerize at the cathode. Polymers were of low molecular weight and were shown to have a polyene structure by infrared and nuclear magnetic resonance spectroscopy. Observations of color development, polymer migration into the anode compartment, and a high sensitivity to moisture suggest an anionic mechanism of polymerization.

Copolymers of phenylacetylene and benzonitrile were observed to form in the cathode compartment in a manner similar to polyphenylacetylene. It was observed that while initial monomer ratios varied greatly, elemental analysis indicates incorporation of monomers in approximately one to one ratio in the resulting copolymer. This observation and the very low molecular weights of the copolymer products suggest that addition of a benzonitrile unit inhibits further polymerization.

The electropolymerization of monomers containing an aziridiny ring was shown to polymerize at the anode, the resulting polymers having a polyamine backbone structure. A cationic mechanism of polymerization was suggested. In addition, a difunctional monomer 2-(1-aziridiny)ethyl methacrylate, was shown to undergo selective polymerizations of the aziridiny group at the anode and the vinyl group at the cathode, leaving unreacted vinyl and aziridiny groups, respectively, in the resulting polymers.

Electrochemical polymerization and deposition offer a new route for coating carbon fibers prior to embedding them in a polymer matrix. The potential value of these techniques to composite property modification was amply demonstrated.

(Portions not supported by ONR were omitted from this abstract).